

SIMULATION OF CATION-WATER FLUX COUPLING
IN IONIC CONDUCTING POLYMERS WITH THE
GENERALIZED NERNST-PLANCK EQUATION

Pierre SCHAETZEL* and Silvia

ALEXANDROVA

*Laboratoire de Thermodynamique des Procédés
IUT, Boulevard Maréchal Juin, 14032 CAEN
CEDEX - FRANCE e-mail
pschaetzel@iutcaen.unicaen.fr

The influence of the structure (swelling and fixed charges concentration) on the diffusion properties of ion conducting materials is not well understood. In this paper we analyse the variation of the diffusion coefficient of the counter-ion and of water and of the cation-water flux coupling coefficient (as defined in the generalised Nernst-Planck equation) when the structure of the material changes.

The multicomponent Nernst-Planck (1) equation used in the simulation is compatible with the diffusion Stefan - Maxwell equation and the heterogeneous Spiegler equation. To simulate the influence of the structure of the ionic conducting polymer we use the dusty gas model: the diffusion coefficients used here are those calculated and published by Schaetzel et al. (2) from self-diffusion, electroosmosis and electrical conductivity experiments.

We show that, at constant swelling of the ion conducting polymer, when the concentration of the ionic fixed charges increases the diffusivity of water is constant, the diffusion coefficient of the counter-ion and the ion-water coupling coefficient decrease sharply. At constant ion exchange capacity of the ion conducting material when swelling increases, diffusivity of water and of the counter ion, and the coupling coefficient increase.

We finally compute the transport number of water and the electrical conductivity of the material with the generalised Nernst-Planck equation. We show that electrical conductivity is little affected by swelling but sharply increases with exchange capacity. Electroosmosis decreases sharply with exchange capacity and increases with swelling.

1) P. Schaetzel and B. Auclair, ,
Electrochimica Acta, 43(21-22), 3375-3377
(1998) 2) P. Schaetzel, E. Favre, B.

Auclair, Q.T. Nguyen, , Electrochimica
Acta, 42(16), 2475 - 2483 (1997)

An expression of the diffusion coefficient of a species in a multicomponent mixture is given and the coupling coefficient between two diffusing species is defined. The coupling coefficients are not symmetrical. We show that the self diffusion coefficients and the diffusion coefficients have very different values.

key words: diffusion, Fick's law, electrolyte, multicomponent mixture, Nernst - Planck equation

Introduction

The Nernst - Planck equation is the expression of Fick's equation in electrolyte solutions or solid electrolytes (for example, in ion exchange membranes). In this short communication, we derive the expression of the Nernst - Planck diffusion equation in a multicomponent solution by rearranging the generalized Stefan - Maxwell equation and show that the expression used in general leads to serious misunderstandings concerning the diffusion coefficients (which are sometimes understood as the self diffusion coefficients) and the flux coupling coefficients which are usually put equal to unity.

Derivation of the multicomponent Nernst - Planck equation

The generalized multicomponent Stefan - Maxwell equation can be written[1]:

$$-\frac{\nabla \mu_i}{RT} = \sum_{j=1}^{j=n} \frac{c_j}{c D_{ij}} \left[\frac{J_i}{c_i} - \frac{J_j}{c_j} \right] \quad \text{with}$$
$$c = \sum_{j=1}^{j=n} c_j \quad (1)$$

J_i is the average diffusive molar flux of species i , n the number of species in the mixture, c_i the molarity of species i , R the ideal gas constant, T the absolute temperature and $\nabla\mu_i$ the gradient of the generalized chemical potential. The D_{ij} are generalizations of Stefan-Maxwell diffusivities and have the symmetrical property ($D_{ij} = D_{ji}$). Rearranging this equation leads to the generalized Nernst - Planck equation:

$$J_i = -c_i D_i \frac{\nabla\mu_i}{RT} + x_i \sum_{j=1, j \neq i}^n \alpha_{ij} J_j \quad (2)$$

with

$$D_i = \frac{c}{\sum_{j=1, j \neq i}^n \frac{c_j}{D_{ij}}} \quad \text{and} \quad \alpha_{ij} = \frac{D_i}{D_{ij}} \quad (2')$$

Eqn. (2') defines clearly D_i as the diffusion coefficient of the i species in the multicomponent mixture. This coefficient is different from the self (or isotope) diffusion coefficient defined by [2]:

$$D_{i^*} = \frac{c}{\sum_{j=1}^n \frac{c_j}{D_{i^*j}}} \quad (3)$$

i^* is the isotope species. We define α_{ij} as the coupling coefficient between J_i and J_j . This coefficient does not have the symmetrical property ($\alpha_{ij} \neq \alpha_{ji}$).

Illustrative example

An illustrative example is needed to show extent to which the usual modified Nernst - Planck equation used to describe diffusion - convection in ion - exchange membranes is not appropriate. Schaetzel et al.[2] have shown that the dissipation in this type of dense material is completely of the diffusive type and that viscous effects are negligible. The example studied here is a polymeric ion exchange material with carboxylate acidic ion exchange groups. The transport properties of this material were precisely described by Despic and Hills [3]. The Stefan - Maxwell equation

explains quantitatively the transport properties in this ion exchange material at variable swelling and ionization [2]. Index 1 holds for the sodium counter ion, 2 for the coion (which has a negligible concentration in the reported experiments), 3 for water, 4 for the ionized ion exchange groups and 5 for the non ionized ion exchange groups. We have computed the diffusivities (D_1 , D_3 and D_{1^*}) and the coupling coefficients α_{13} and α_{31} from the calculated mutual diffusivities computed by Schaetzel et al. (fig. 1 and 2) based on the experimental results reported by Despic and Hills [3]. On Fig. 1 and 2 the concentration of the counter ions is represented by the degree of ionization (y_1) which is the ratio between the ionised and the total functional groups.

Discussion

The usual modified Nernst - Planck equations used in the pseudo-binary case (water plus counterions in an ion - exchange membrane) when neglecting convection are:

$$\begin{aligned} J_1 &= -c_1 D_1 \frac{\nabla\mu_1}{RT} + x_1 [J_1 + J_3] \\ J_3 &= -c_3 D_3 \frac{\nabla\mu_3}{RT} + x_3 [J_1 + J_3] \end{aligned} \quad (4)$$

In this equation, x_1 represents the mole fraction of the counter - ion in the binary liquid mixture. The result for the generalized Nernst - Planck equation leads to:

$$\begin{aligned} J_1 &= -c_1 D_1 \frac{\nabla\mu_1}{RT} + x_1 \alpha_{13} J_3 \\ J_3 &= -c_3 D_3 \frac{\nabla\mu_3}{RT} + x_3 \alpha_{31} J_1 \end{aligned} \quad (5)$$

In this case, x_1 represents the mole fraction in the ternary mixture and fig. 1 shows that the coupling coefficient α_{13} is clearly different from unity and is not symmetrical. So, the usual and the generalized Nernst - Planck equations are quite different.

We show now how the diffusion coefficients and the coupling coefficients can be measured in an ion exchange membrane (with total Donnan exclusion), from three simple transport experiments: electroosmotal flux, hydraulic permeability and electrical conductivity. From equation (5),

we see that the product $\alpha_{31} \times_3$ is the transport number of water. The D_3 coefficient can be computed from the hydraulic membrane permeability ($D_h = J_3 V_3 / (-dp/dz)$) at nil electrical potential gradient and concentration gradient). The result is:

$$D_3 = \frac{D_h RT}{c_3 V_3^2} \tag{6}$$

V_3 is the partial molar volume of water. D_{13} ($= D_{31}$) is computed from eqn. (2'). The electrical conductivity (λ) measurement leads to the calculation of D_1 :

$$\lambda = \frac{F^2 D_1 c_1 Z_1}{RT \left[1 - x_1 x_3 D_1 D_3 / D_{13}^2 \right]} \tag{7}$$

α_{13} is obtained by eqn..(2') i.e. $\alpha_{13} = D_1/D_{13}$.

Historically, one of the reasons for the introduction of convective flow in the Nernst - Planck equation is the discrepancy between the calculated and the measured water transport number: in fact, a polymer ion - exchange membrane should be considered as a dense membrane (i. e. a pore free membrane) where the convective flow can be neglected. The correct equation to be used should be the multicomponent diffusion Nernst - Planck equation developed in this paper. Another early error in this field has been the use of the self-diffusion coefficient in place of the diffusion coefficient. For the illustrative example, Fig. 1 shows that the self-diffusion coefficient is about 20% lower than the diffusion coefficient defined by equation (2').

Bibliography

1. E.M. Scattergood and E.N. Lightfoot, Trans. Faraday Soc., 64 (1968) 1135.
2. P. Schaetzel et B; Auclair, Electrochimica Acta, 38(1993)329.
3. A. Despic and G.J. Hills, Trans. Faraday Soc., **21** , 150 (1956).
4. P. Schaetzel, E. Favre, B. Auclair et Q.T. Nguyen, Electrochimica Acta, 42,16(1997)2475.

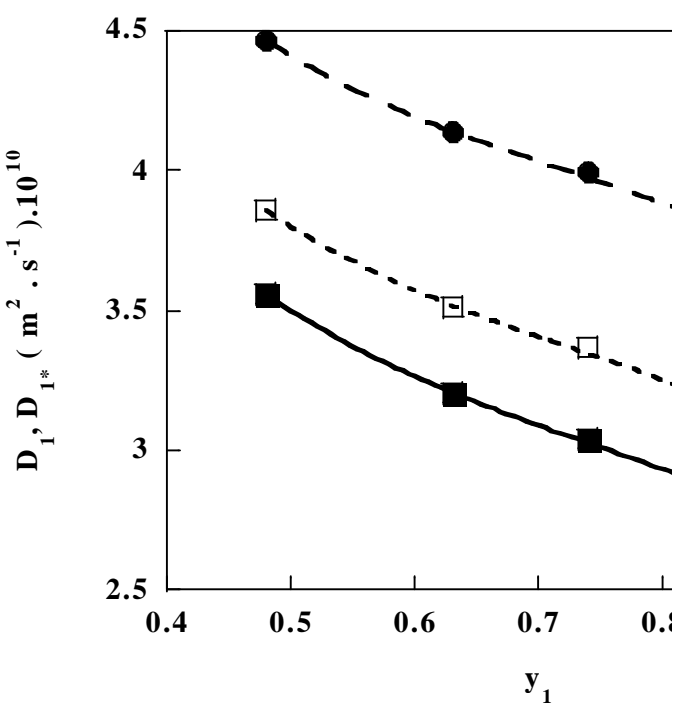


Fig. 1

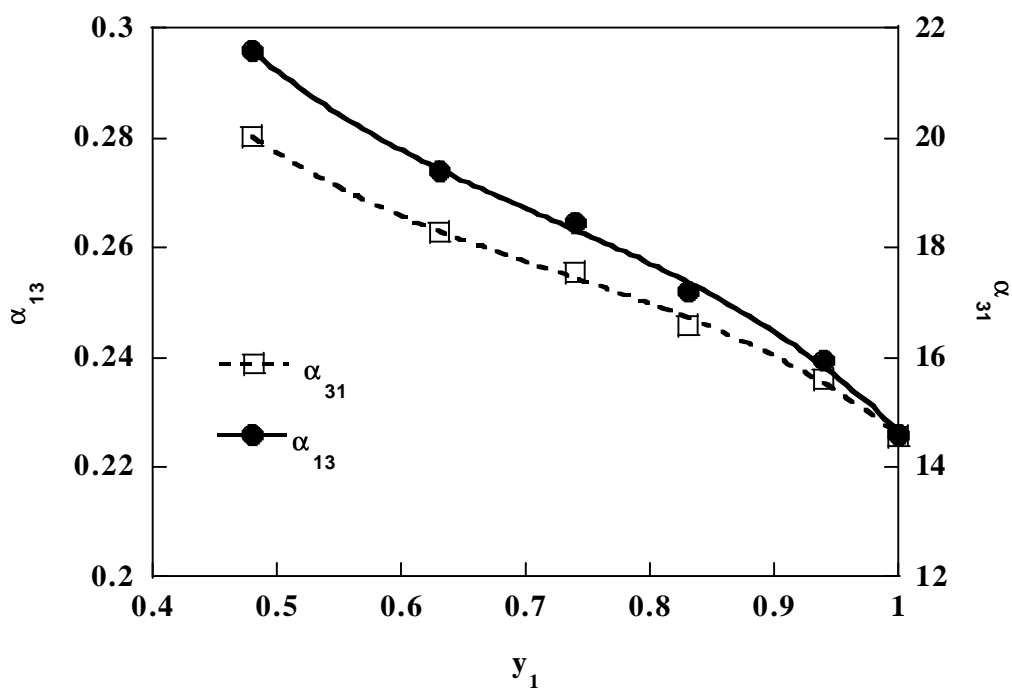


Fig. 2

List of figures

Fig. 1 Diffusion coefficients of the sodium ion (D_1), of water (D_3) and self diffusivity (D_{1*}) of the sodium ion vs. neutrality rate in the polymer calculated from [2].

Fig.2 Coupling coefficients α_{13} (sodium ion - water) and α_{31} (water - sodium - ion) vs. neutralization rate in the polymer [2,3,4]